Spectroscopic study of the local chemical environment during biotransformation of uranium

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Previous studies [1] have identified changes in uranium solubility in sediments as a result of processes such as uranium reduction, microbial activity or ion exchange. In that study, radionuclide and microbiological analyses have demonstrated changes in uranium solubility and shifts in biological profiles in response to nitrate reduction. However, there was no direct information on local structure and oxidation states of uranium so this has been studied using X-ray absorption spectroscopy (XAS) to define speciation changes.

Microcosms (50 mL; 20 g sediment) containing 100 ppm and 2000 ppm of uranyl ion in solution were set up with nitrate as TEA. EXAFS spectral data were collected before and after reduction of nitrate. The data obtained showed the presence of uranyl ion both before and after nitrate reduction and in both solution and solid phases, showing that this process was not associated with uranium reduction [2,3]. The uranium speciation changes can be related to formation of either dihydroxy-bridge oligomeric species or uranium-carbonato complexes [4].

[1] Al-Bokari *et al*. (2007) *Environmental Radiochemical Analysis III* **312**, 95-100. [2] Kelly *et al.* (2003) *Advance Photon Source*, Activity Report. [3] Moyes *et al*. (2000) *Environmental Science & Technology* **34**, 1062-1068. [4] Walter *et al*. (2003) *Environmental Science & Technology* **37**, 2898-2904.

Silicate weathering in anoxic marine sediments: Detailed mineralogical investigation

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The continental weathering of silicates is known to be the largest sink of atmospheric CO_2 on geological timescales. Recent studies have shown that silicate weathering processes also take place naturally in the marine environment (Wallmann et al. 2008 [1]).

In order to study these processes anoxic sediments from the northern slope of Sakhalin Island, Sea of Okhotsk, were analyzed for their mineralogical and geochemical composition. The resulting down-core trends in mineral abundance suggest a transformation of reactive silicate phases (e.g. plagioclase, pyroxene) into cation-depleted silicates due to reactions with CO_2 produced during methanogenesis.

Further detailed mineralogical analyses were conducted in this study by means of smear-slide counting, electron microprobe analysis, and XRF of the clay fraction. The results show a variety of reactive and refractory minerals in the silicate phase, whereas mineral trends imply down-core decreasing abundances. The main component, being reactive plagioclase, decreases down-core from 7 to 4.5 %.

The data will now be used to extend an existing transport-reaction model for silicate weathering by incorporating the individual mineral phases, and will thus help to quantify individual rates of singular phases. This will improve our understanding of the naturally occurring neutralization of CO_2 and constrain the timescales of mineral trapping during CO_2 sequestration.

[1] Wallmann et al. (2008) *Geochim. Cosmochim. Acta* **72**, 3067-3090.